# SORPTION REFRIGERATION DEVELOPMENT 1747/145%

Jack A. Jones
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

**Key** Lecture Presentation in "Heat Pipes, Heat Pumps and Refrigerators"

CIS Countries Association

Luikov Institute, Minsk, Belarus, September 12-13, 1995

## **ABSTRACT**

The Jet Propulsion Laboratory (JPL) has been involved in cryogenic refrigeration development for the National Aeronautics and Space Administration (NASA) since 1979. With the help of NASA, Southern California Gas Company, Ford Automotive, and Aerojet General, we have spun off this technology for commercial air conditioning since 1990. In all, JPL has fabricated and successfully tested the following sorption refrigerators: physical solid adsorption systems (helium, nitrogen, krypton, R22, R134a, and ammonia), chemical solid absorption systems (hydrogen, nitrogen, and oxygen), and liquid absorption systems (ammonia and R1 34a). Two hydrogen chemisorption systems for cooling to 10 K (-263 'C) and 2S K (-248 "C) are presently flight qualified and ready to cool detectors for a NASA Shuttle mission and a National Science Foundation (NSF) Balloon Flight.

All of these systems operate on the same **basic** principle of absorbing a refrigerant gas at a lower temperature, typically near room temperature, and then **desorbing**, or venting, the gas at a much higher pressure when heated an additional 100 to 200 'C. Precooking and expansion of **the** gas then **creates** refrigeration with essentially no wear-related moving parts.

Of particular interest are two commercial developmental projects. One system being built by Aerojet and licensed from JPL/Caltech, is a 7.2-ton solid adsorption air conditioner that will be installed on a subway train in Los Angeles. This system will be powered by the waste heat from the train's electro-resistive braking system, and is scheduled for completion in 19%. Another sorption project being pursued by Ford Automotive and the Southern California Gas Company at JPL is the development of high performance, compact liquid absorption systems that can be powered by gas heat or automotive exhaust waste heat. Although the performance projections are not quite as high as those for the solid adsorption systems, the liquid R134a and ammonia absorption compression systems are extremely simple, inexpensive, and light weight. Furthermore, the systems are insensitive to gravity vector changes, thus potentially fitting some mobile heat-activated applications, where some performance can be sacrificed, but cost is critical.

## **BACKGROUND**

Since 1979, JPL has been involved in the development of cryogenic cooling systems for the cooling of infrared sensors used by NASA and the U.S. Department of Defense. In particular, JPL has been a leader in the development of solid sorption cryogenic refrigeration systems to provide cooling of infrared detectors for long life outer-planet missions, as well as for earth-orbiting surveillance missions, Sorption compressors operate by sorbing a low pressure refrigerant onto solid powders, typically near room temperature, and exhausting the refrigerant at high pressures when the powder is heated an additions! 100 to 200 °C. When the high pressure refrigerant is precooled and expanded, it provides net refrigeration. Thus, simple heating and cooling of the powders provide a solid-state cooling system with essentially no wear-related moving parts. The basic operation is shown in Figure 1, which has two sorbent beds heisting (outgassing high pressure refrigerant) and two sorbent beds cooling (adsorbing iow pressure refrigerant). Expansion of the precooled refrigerant through an expansion valve, or orifice, provides cooling.

### SORBENT/SORBATE COMBINATIONS

In general, there are four broad categories of sorption refrigeration research that have been conducted at JPL. These are cryogenic sorption refrigeration (physical and chemical) and air conditioning sorption refrigeration systems (solid adsorption and liquid absorption). A summary of the sorbent/sorbate combinations actually tested is shown in Table 1.

Cooling Category	Sorption Type	Types Tested at JPL
cryogenic	Physisorption	C/N <sub>2</sub> , C/Kr, C/H <sub>2</sub> , C/He
	Chemisorption	LaNi <sub>4.8</sub> Sn <sub>0.2</sub> H <sub>2</sub> , LaNi <sub>5</sub> /H <sub>2</sub> , ZrNi/H <sub>2</sub> , PrCeOx/O <sub>21</sub>

Air Conditioning Physical Adsorption

Liquid Absorption

'Table 1. Sorption Combination Testing at JPL

# A. Cryogenic Physiosorption Systems

C/NH<sub>3</sub>, C/R2Z, C/R134a H<sub>2</sub>O/NH<sub>3</sub>, Solvent/R134a

JPL has built and tested activated carbon/nitrogen (C/N<sub>s</sub>) systems for operation in the 100 to 120 K range<sup>(1)</sup>, C/Hz for 20 to 30 K cooling, and C/He for 4-5 K cooling. These systems have somewhat limited applicability, however, since the C/Nz system requires heatsinking to 225 K or below, while the C/Hz system requires 80 K or below, and the C/He system requires heat rejection at 20 K or below. Another cryogenic physiorption system tested at JPL is a C/Kr system<sup>[3]</sup> for cooling in the 135 to 140 K region, when cooled to at least 275 K. This system is quite viable, especially as an upper stage cooler for an oxide chemiosorption system (as will be discussed in a later section). Over 16,000 hours of operation were accumulated cm a C/Kr system at JPL<sup>[4]</sup>.

### B, Cryogenic Chemisorption Systems

Among the cryogenic cooling chemisorption systems tested are hydrides with hydrogen, PrCeOx/O<sub>2</sub> (PCQ/O<sub>2</sub>) and Mn/N<sub>2</sub>. Due to the very high temperatures required for the Mn/N<sub>2</sub> reactions<sup>(3)</sup>, generally above 800 "C, this system has seen little practical use, thus far. The oxide and hydride systems, however, appear to have far more useful applications. The hydride work was begun at JPL in 1979 and was modeled after work done by Van Mal et all<sup>(5)</sup> in the early 1970's.

In the early 1980's, JPL fabricated and endurance tested a LaNi<sub>3</sub>/H<sub>2</sub> refrigerator<sup>[7]</sup> for cooling to 20 to 30 K. This initial testing lasted about 500 hours and was followed by 3,000 cycles of operation on a LaNi<sub>4.5</sub>Sn<sub>0.5</sub>/H<sub>2</sub> system and 3,000 hours of operation on a ZrNi/H<sub>2</sub> system<sup>[4]</sup>. These latter two systems have been developed as a 25 K and 10 K stage, respectively, for a U.S. Defense Program mission that is scheduled to fly on the Space Shuttle in December 1995.

The final cryogenic cooling chemisorption system listed in Table 1 is that of praseodymium-cerlum-oxide/oxygen (PCO/O<sub>2</sub>). This unusual combination was originally discovered by Mulhaupt<sup>(f)</sup> (Union Carbide) to be of value in chemically separating oxygen from nitrogen in air. JPL Ker tested this combination and found that it was uniquely qualified for providing cooling in the 65 to 9 K temperature region<sup>(P)</sup>. This system requires a heat source of about 600 °C with a heat rejection temperature of about 450 °C. A PCO/O<sub>2</sub> system was built and tested at JPL and accrued about 36,000 hours (80,000 cycles) of maintenance-free operation with no measurable performance degradation.

Another LaNi<sub>4.8</sub>Sn<sub>0.4</sub>/H<sub>2</sub> system has been fabricated for a 25 K cooler on a National Science Foundation Balloon Astronomy flight scheduled for the Arctic late in 1995,

Of particular interest in the oxide system is the use of a C/Kr stage for precooking the oxygen. This is shown schematically in Figure 2, with a thermoelectric cooler (TEC) providing precoling to 200 K for both stages. The primary advantage of this type of system is that the PCO waste heat may be used to provide the entire heating requirement for the C/Kr stages. A heat-cascading compressor has, in fact, been designed at JPL (Figure 3), although it has not yet been fabricated. Vacuum gasgap thermal switches separate the PCO/O<sub>2</sub> and Kr/O<sub>2</sub> stages from an outer heat rejection jacket.

# C. Adsorption Air Conditioning

For ground air conditioning applications, activated carbon has been used with ammonia, R22, and R134a as sorbates. In general, the simple sketch of Figure 1 has been found to be too inefficient to compete with alternate heat pump technologies. To conserve energy, a number of heat regeneration techniques have been attempted, whereby the waste heat from the sorbent bed is used to heat another sorbent bed. Shelton<sup>103</sup> and Tchernev<sup>[11]</sup> have devised a simple double-bed system, in which a hot sorbent bed that is being cooled will pass its heat to a coolant fluid which then passes through a heater (to makeup for regeneration thermal losses) and then onto another sorbent bed. A number of alternate techniques using four, six, or more beds have also been proposed. [12,13]

Extensive studies have been performed at JPL, which show that a four-bed approach is much more efficient than two beds, but that there is not a significant advantage in using more than four beds. [14,15] In particular, a patented four-bed approach (Figure 4) will use a fluid (water or oil) to transfer hot and cold thermal waves. [16] In addition, it has been discovered that significant performance improvement can be attained if the coolest sorbent bed is sled further at the end of each quarter cycle without regenerating the fluid through the other three sorbent beds. With this type of "bottoming," the JPL models have predicted a coefficient of performance (COP) of 1.0 for a 3S 'C day using ammonia adsorbed on activated carbon, The COP, using Freon-12 replacement fluid R134a, has been predicted to be about 0.8. These predicted efficiencies are higher than any other single stage heat-powered air conditioning systems presently on the market.

In order to confirm the analytical tools, a single compact sorbent bed was fabricated and tested in both heating and cooling modes. The sorbent bed (Figure 5) consisted of activated carbon with a binder that was molded into a finned aluminum tube extrusion (patent pending<sup>[17]</sup>). Pressurized water was selected as the heating and cooling means. A hollow ullage volume in the center of the water stream allowed enhanced fluid heat transfer @efficient.s. The transient thermal test results showed very good correlation to analytical predictions, [15] although full system COP was not able to be measured with only one sorbent bed. Of the three refrigerants that were tested (R22, R134a, and ammonia), ammonia was almost three times superior to the others and yielded 1038 BTU/hr (304 W) cooling for only a 0.51 kg carbon bed.

This technology<sup>[16,17]</sup> has now been spun off and is being licensed by Aerojet General to provide 7.2 tons (25.3 kW) of air conditioning for a Los Angeles County subway car. For this application, the entire compressor heater power will be derived from the subway train's electroresistive brake waste heat. The subway car sorption air conditioning installation is scheduled to occur in 19%. This same technology is also being evaluated by Aerojet to provide high-efficiency air conditioning systems for home and commercial applications,

# D. Liquid Absorption Air Conditioning

Liquid absorption systems perform very similarly in principle to solid sorption systems, **except** that the liquid **moves** through the unit. A typical liquid absorption system is shown in Figure 6. **Low** pressure ammonia is absorbed into water in the absorber part of **the** unit. It is then pumped to a high pressure and passes through a **heat** exchanger into a hot gas generator section. The

ammonia **desorbes** at high pressure from **the** water, and most of the water vapor is distilled out of the ammonia **in** the rectifier. The depleted liquid solution **then** passes back to the absorber where it is **cooled** and ready **to** absorb low pressure ammonia.

Liquid absorption systems have both advantages and disadvantages compared to **solid** sorption systems. For ammonia systems, water will absorb about three times as much ammonia by weight as **the best carbon** adsorbent. Although heat transfer is easier for **liquid** systems, the mass transfer of **refrigerant** back into liquid solution is more difficult. A very large **cooled** surface area is typically required to enhance liquid/gas absorption, and this surface area is usually very sensitive to motion **and/or** gravity.

**Recently**, the Southern California Gas Company funded JPL to develop a high performance liquid absorption system that can be compact enough to fit into a typical window unit air conditioning unit for cooling multiunit dwellings, JPL has now fabricated a bench-model, proof-of-principle liquid absorption unit that may be compact enough for window air conditioning units.

The actual design is still proprietary, but the unit promises to be low cost, lightweight, reasonably efficient, and motion insensitive. Preliminary tests will be performed in 1995 using a water/ammonia combination in the apparatus. Subsequent funding by Ford Automotive will have allowed testing of R134a absorbed into a number of organic solvents. The intent is to develop air conditioning units for cars that can be powered by automotive exhaust waste heat.

Although all testing is to be performed in a stainless **steel** apparatus, actual **commercial** fabrication of ammonia units would **consist** of mild steel with appropriate **corrosion** inhibitors. **R134a** units could be fabricated from inexpensive **aluminum** alloys.

## SUMMARY AND CONCLUSIONS

JPL has long recognized the virtues of sorption refrigeration for long-life, maintenance-free and vibration-free operation in space. One cryogenic sorption system that looks particularly attractive is PCO/O<sub>2</sub> for chemisorption cooling to 65 to 90 K, especially with a C/Kr physisorption upper stage that can be powered entirely by the PCO waste heat. Another sorption cryogenic combination that looks especially attractive and that will be flown in the Space Shuttle later this year is a LeNi<sub>4</sub>, Sn<sub>0.2</sub>/H<sub>2</sub> system for cooling to 25 K, with a ZrNi/H<sub>2</sub> system for cooling to 10 K. All of the above systems, fabricated for NASA and the U.S. Defense Department, have been life-tested for many thousands of hours at JPL, and all can have heat rejection temperature at about room temperature or above.

In the area of physical adsorption air conditioning, one system that has been recently tested at JPL and that looks very attractive is a carbon/ammonia (C/NH system that uses a water fluid loop to regenerate waste heat from one C/NH, sorption compressor to the next. Recently this system was licensed to Aerojet Corporation, and a 7.2 ton (24.6 kW) system will be fabricated for the Los Angeles County Metrorail Subway System, Special safety features are being incorporated to prevent any accidental leakage of ammonia from the system.

In the area of **liquid** absorption refrigeration, systems that use **H<sub>2</sub>O/NH<sub>3</sub>** and **Solvent/R134a** are being tested at JPL. Although these absorption system designs are proprietary, some improvements **over conventional** absorption systems include significant miniaturization and **cost reduction in** the absorber **generator**, and **heat** transfer/mass transfer **areas**. Potential applications **for** the **H<sub>2</sub>O/NH<sub>3</sub> system** are **for** use in window **air** conditioners, and for the **Solvent/R1** 34a system are for **use** in exhaust-heat **powered** air **conditioning** for automobiles.

### ACKNOWLEDGMENTS

The research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA).

Funding **for** the cryogenic sorption work has been provided by NASA, the United **States** Air Force, the U.S. Strategic Defense Initiative Organization, and the U.S. Ballistic Missile Defense Organization. Funding for the sorption air conditioning work **has** been provided by NASA, Southern California Gas Company, **Aerojet** Corporation, and Ford Motor Company.

# REFERENCES

- 1. Bard, S. Development of an 80-120 K Charcoal—Nitrogen Adsorption Cryocooler, paper presented at Fourth Bienniel Int. Cryocooler Conf., Easton, Maryland, USA (September 1986).
- **Chan,** C. K., Performance of Long Life Joule–Thomson **Cryocooler**, paper presented at Interagency Meeting on **Cryocoolers**, **Easton**, Maryland, USA (1986).
- 3. Bard, S., Jones, J. A. and Schember, H. R., A Two Stage 80/140 K Sorption Cryocooler, Proc. ICEC 12 Butterworths, Guildford, UK (1988).
- 4. Bard, S., J. Wu, P. **Karlmann**, C. **Murate**, and L. Wade, 'Component Reliability Testing of Long-Life Sorption **Cryocoolers**," 8th International **Cryocoolers Conf.**, Vail, Colorado, June 28-30, 1994.
- 5. Jonas, J. and Alan Lund, "Manganese Nitride Isotherms for Sorption J.T. Refrigeration," Advances in Cryogenic Engineering, Vol 35, 1990.
- 6. Van Mal, H. H. and Mijnheer, A., Hydrogen Refrigerator for the 20 K Region with a LaNi, Hydride Thermal Absorption Compressor for Hydrogen, Proc ICEC 4 IPC Science and Technology Press, Guildford, UK (1992).
- 7. Jones, J. A. and Golben, P. M., Design, Life Testing and Future Designs of Cryogenic Hydride Refrigeration Systems Cryogenics (1985) 25212.
- 8. Mulhaupt, J. T. Process and Composition for Separation of Oxygen from Air Using FC Oxides as the Carrier, U.S. Patent No. 3980 ???????? (September 1970).
- 9. Jones, J. A. Oxygen Chemisorption Cryogenic Refrigeration U.S. Patent No. 4697425 (October 1987).
- 10, Shelton, S. V., Wepfer, W. J., and Miles, D. J., "Square Wave Analysis of the Solid-Vapor Adsorption Heat Pump)" *Heat Recover Systems & CHP*, No. 3, pp. 233-247, Great Britain (1989).
- 11. **Tchernev,** D. and Emerson, D., "Closed Cycle **Zeolite** Regenerative Heat Pump," 2nd International Workshop on Research Activities of **Advanced** Heat Pumps, **Graz**, Austria (September 1988).

1

- 12. Miller, E. B., "The Development of Silica Gel Refrigeration," Refrigerating Engineering, Voi. 17, NO. 4, pp. 103-108 (1929).
- Wade, L., Alvarez, J., Reyba, E., and Sywulka, P., "Development of a High Performance Sorption Refrigerator," paper presented at Space Cryogenics Workshop, California Institute of Technology, Pasadena, California (August 1989).
- 14. Jones, J. A. and Vassilis Christophilos, "High Efficiency Regenerative Adsorbent Heat Pump, ASHRAE Winter Annual Meeting, Chicago, Illinois (January 1993).
- **1s.** Jones, J. A., "Sorption Refrigeration Research at **JPL/NASA,"** Solid Sorption Refrigeration Conference, Intonational Institute of Refrigeration, Paris, France (November 18-20, 1992).
- **Jones**, J. A., "Regenerative Adsorption Heat Pump," U.S. Patent No. 5,046,319, Jet **Propulsion** Laboratory, California **Institute** of Technology, Pasadena, California,
- 17. Jones, J. A. and Yavroulan, A., "Activated Carbon Sorbent with Integral Heat Transfer Device," U.S. Patent No. S,388,637, February 14, 1995.